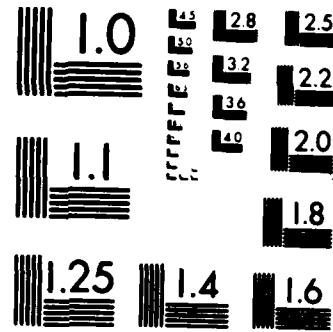


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ION PLATING FOR CORROSION CONTROL

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METALS RESEARCH DIVISION

August 1987

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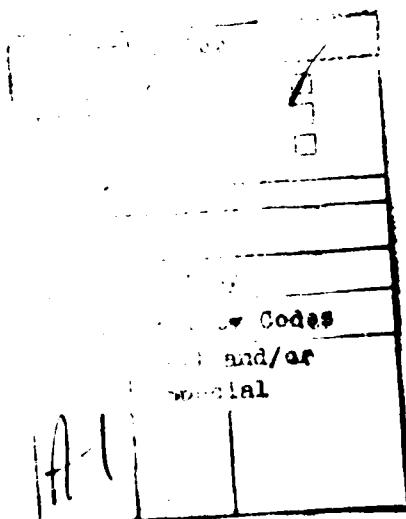
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ABSTRACT

Coatings deposited by ion plating are becoming more widely used for corrosion protection. Aluminum coatings may be the most advanced commercially at this time. Other identified candidates (depending upon the substrate) are iron-chromium, aluminum-magnesium, copper-aluminum, and titanium-nitride. Important characteristics of these coatings are chemical composition and micro-structure. An amorphous or microcrystalline structure can result in vastly enhanced resistance to corrosion for metal films that have an inherent tendency toward passivity. These structures can also lead to the formation of a resistant spinel-type oxide layer in certain alloys. The influence of process parameters in achieving these structures will be discussed.

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INTRODUCTION

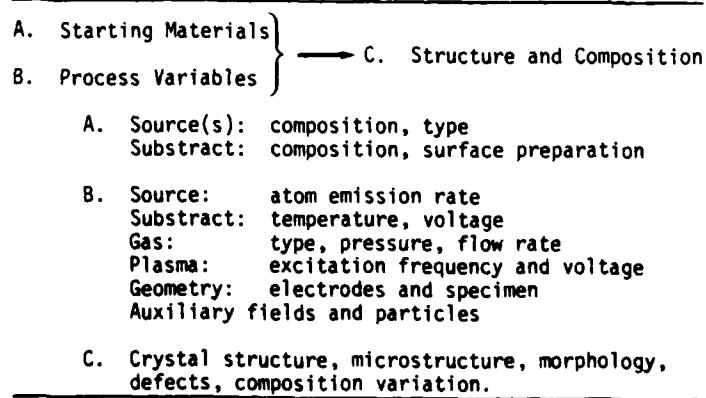
Ion plating may be a preferred technique for depositing corrosion resistant films. This report discusses some of the characteristics of the process and of the ion plated films.

Each of the numerous variations of physical vapor deposition (PVD) techniques for coatings has its distinctive advantages. Many of these variants are used commercially and some cover applications that require resistance to corrosion. There are many forms of corrosion and different corrosive environments. Herein we deal with the general and pitting forms in aerated sodium chloride solutions at room temperature. This is not to say that other forms of corrosion, such as crevice or stress corrosion cracking, are unimportant, but that the available data for ion plated films deal mainly with pitting corrosion in chloride solutions.

A PVD technique closely related to ion plating, and more generally used, is bias sputtering. Here, the material to be deposited is made the cathode (negative) of a glow discharge, and the material to be coated is placed in the plasma and is biased negatively. In ion plating, the substrate is made the cathode and the material to be deposited is thermally evaporated (or, in some cases, sputtered). Advantages of ion plating are: simplicity, excellent adherence (a degree of near-surface atom mixing can be achieved), good throwing power, rapid deposition, relatively benign environmental hazard (compared to electroplating), fairly economical, electrical and mechanical film properties often excellent, and control of microstructure and composition can lead to relatively thin coatings for corrosion protection.

The two key factors on which the corrosion resistance depends are structure and composition. Table 1 lists some of the parameters that influence these factors. Control of film composition may be effected through the use of special sources such as: multiple crucibles, or flash evaporators, or arcs, or sputtering targets, and reactive atmospheres. In some cases, control over residual impurities in the plasma is important.

Table 1. PARAMETERS INFLUENCING STRUCTURE AND COMPOSITION OF ION PLATED FILMS



By manipulation of the deposition parameters one can control the structure of the resulting film. The microstructure of thermally evaporated metal films was correlated by Movchan and Demchisin¹ into several zones dependent upon the homologous temperature of the substrate, T_s/T_m , where T_s is substrate temperature and T_m

1. MOVCHAN, B. A. and DEMCHISIN, A. V., Phys. Met. Metallogr., v. 28, 1969, p. 83.

is the melting point of the film material. Thornton^{2,3} extended this correlation to the structure of sputter-deposited films using both T_s/T_m and the pressure of the Ar sputter gas as independent variables. At relatively high T_s/T_m (greater than about 0.8), Zone 3, an equiaxed structure is produced. At lower T_s/T_m (0.5-0.8), Zone 2, the structure is columnar with dense boundaries and a relatively smooth matte surface. At low T_s/T_m (less than 0.1), Zone 1, a structure of tapered crystallites with domed tops and voided boundaries is formed. Between Zones 1 and 2 is a transition region, Zone T, of dense fibrous grains.

The energy of the particles arriving at the substrate during sputtering and ion plating is much greater than from a thermal evaporation source in high vacuum (a factor of 100 to 1000 or more). An ion bombardment flux is added to the neutral atom coating flux and the structure can be densified, even at low (80eV) ion energies.⁴ To some extent this energy can be substituted for substrate temperature in obtaining adherent films with good properties. Low T_s is not only useful in preserving the substrate structure but is instrumental in obtaining microcrystalline and amorphous films with particularly good corrosion resistance in appropriate circumstances. The adherence is also improved as bombarding ion energy increases, and significant coating-substrate atom mixing can occur at arrival energies over 100eV.⁵ Ion plating provides a convenient method for exchanging arrival energies for substrate temperature. The addition of extra electrical and magnetic fields can enhance the energy distribution.⁶ As will be seen below, lower substrate temperatures, and faster vapor quenching, can improve the corrosion resistance.

CORROSION PROTECTION

There are two general methods by which a coating can protect a substrate: 1) the coating is electrochemically more active than the substrate in the environment, or 2) the coating is less active (more noble). In the first method, the coating is sacrificial, and it will give substantial protection even when porous. Still better protection is obtained if the coating forms a passive layer. In the second method, the coating must be non-porous and robust, otherwise, the environmental attack will be especially vigorous where the substrate is exposed because of the high galvanic current density there. Thus, where possible, the first method with a passive layer is preferred, especially when the active metal forms a passive layer. For either method, ion plating is a useful technique.

Chemical composition of the coating is the primary determinant of the relative substrate-coating nobleness (for a given substrate). Coating structure plays a decisive role in the degree of porosity (especially for thin films about 1μm) and in the degree of passivity. It may be possible with ion plating to modify the zone structure limits so as to achieve denser films at lower T_s than obtained by evaporation or sputtering. At very low T_s microcrystalline and amorphous films can be produced (the latter when additional elements are incorporated in the film), and these will show enhanced passivity over the more common crystalline films.^{7,8,9}

2. THORNTON, J. A., *J. Vac. Sci. Technol.*, v. 12, 1975, p. 830.
3. THORNTON, J. A., *Ann. Rev. Mater. Sci.*, v. 7, 1977, p. 239.
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5. WEHNER, G. K., and ANDERSON, G. S., in *Handbook of Thin Film Technology*, L. I. Maissel and R. Glang, eds., McGraw-Hill, New York, 1970, Chap. 3.
6. SAULNIER, P., DEBHI, A., and MACHET, J., *Vacuum*, v. 34, 1984, p. 765.
7. NOWAK, W. B., *Mat. Sci. Eng.*, v. 23, 1976, p. 301.
8. NOWAK, W. B., and OKORIE, B. A., *Corrosion*, v. 38, 1982, p. 314.
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Figure 1 shows a potentiodynamic polarization curve of bulk 304 stainless steel taken in 1M NaCl aerated, near-neutral aqueous solution at room temperature. The passive region (constant current density 10^{-7} A/cm 2) extends 100mV above the corrosion potential, E_c , of -168mV(SCE). Figure 2 shows a similar polarization curve for a microcrystalline 304 stainless film (1μm thick) sputter deposited onto a substrate held at about 77K (liquid nitrogen). E_c is -140mV(SCE) and the passive region at 10^{-7} A/cm 2 extends for 250mV. Small additions (1 at.%) of co-sputtered Al and Si to the 304 stainless films resulted in $E_c = -160$ mV and a passive length of 330mV at 10^{-8} A/cm 2 . The increased length of the passive region and the decrease in passive current indicate greater resistance to pitting and to general corrosion. The structure of the co-sputtered film was determined by transmission electron microscopy and diffraction to be duplex: 15-30nm sized particles in an amorphous matrix. The primary effect of the added Al and Si is to change the microstructure which, in turn, leads to a more uniform passive layer. A graphic demonstration of this passivity was the extreme difficulty in removing these films from stainless steel substrates or from glass slides by using stainless steel chemical etchants.

Ion plated Fe-Cr-P-B films, Cr content above 8%, have yielded amorphous structures with $E_c = +150$ mV(SCE), passive current density about 2×10^{-7} A/cm 2 , and a passive region 600-700mV long.¹⁰ This indicates extraordinarily good corrosion resistance to the saline environment. If this film were porous, its excellent protective capability would depend upon its being more active than the substrate. The corrosion resistance of the Fe-Cr alloys depends upon the formation of a very thin (103nm) layer of hydrated chromium oxyhydroxide¹⁰ and the superior resistance of the amorphous form of these alloys is due to homogeneity of the alloy, which leads to homogeneity of the oxide barrier.

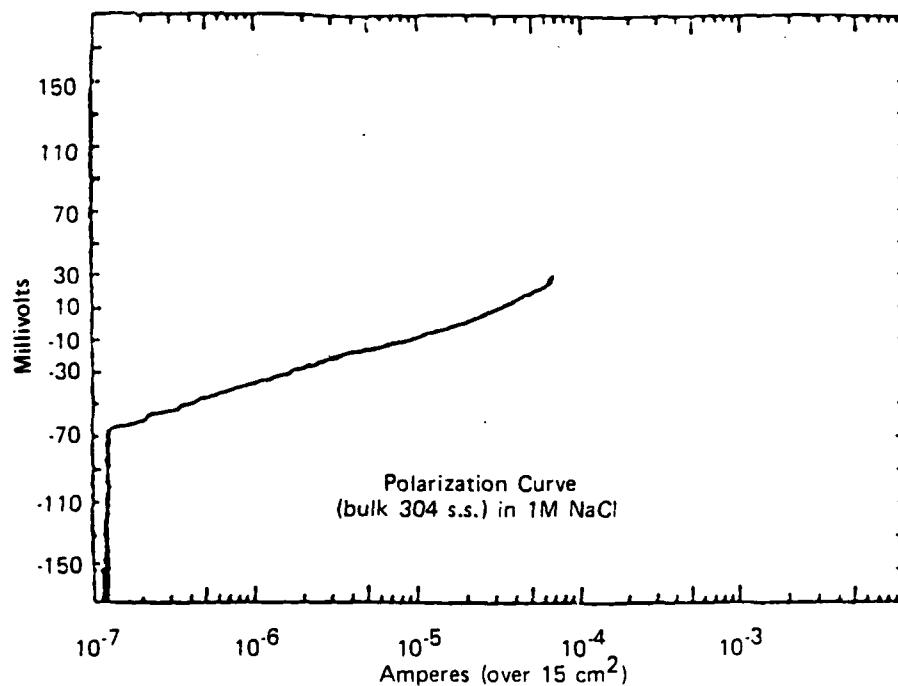


Figure 1. Polarization curve of bulk 304 stainless steel (Ref. 7).

10. MASUMOTO, T., and HASHIMOTO, K., Ann. Rev. Mat. Sci., v. 8, 1978, p. 215.

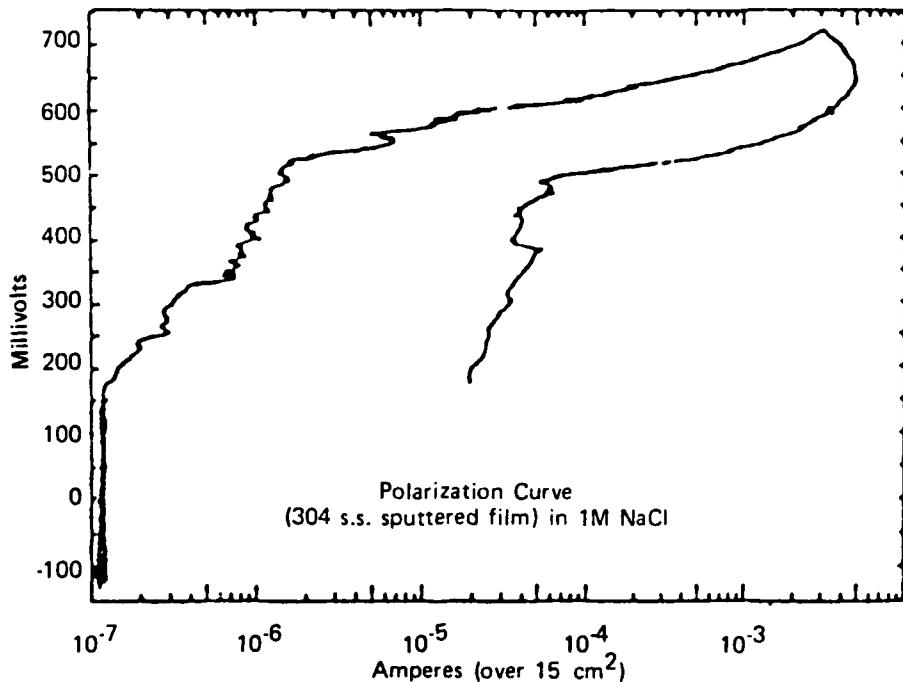


Figure 2. Polarization curve of 304 stainless steel sputtered thin film (Ref. 7).

Another way to achieve very good corrosion protection is to use a metal alloy that will form an oxide of the spinel structure in the corrosion environment.¹¹ This has been achieved with ion plated Al-Mg alloys having a microcrystalline structure.¹² Rapidly quenched ribbons of alloys with composition similar to the ion plated films have 50-200% higher passive current densities, have lower pitting potentials, and have a 2 to 3 times shorter passive region than the ion plated films; thus, the films are more corrosion resistant than the ribbons in a 3.5% NaCl aerated, near-neutral solution at room temperature. In contrast to conventional bulk Al-Mg alloys in the equilibrium two-phase region, the ion plated films form a spinel oxide.

Recently, ion plated TiN has been shown to have superior corrosion resistance in 1N H₂SO₄ solution, as compared to sputtered TiN or N-implanted sputtered Ti.¹³ The ion plated TiN showed a passive region of over 750mV at a current density of 10⁻⁶ A/cm².

Attempts have been made to protect a tungsten alloy with thin ($1\mu\text{m}$) ion plated films of Al, Fe₈₀Ni₁₅Cr₅, and Al₆₉Ni₃₁. The substrate temperature was near 77K, so the films were probably microcrystalline, but also microporous. The iron alloy was slightly more noble than the tungsten in 3.5% saline solution, and the other two were appreciably less noble; all had anodic passive regions at about $2 \times 10^{-5} \text{ A/cm}^2$. After 3 weeks of immersion in 5% saline solution at room temperature the iron alloy film had disappeared, the Al film had not protected the tungsten (a black corrosion product was visible), but the Al-Ni film was intact. The failure of the more noble microporous iron alloy film is understandable. It is not clear why the Al film failed to protect. On the other hand, the most active Al-Ni is probably protective because a spinel oxide layer may have formed. No corrosion was noted for any of these films after a two-week exposure to air at 115°F and 90% relative humidity.

11. ERDEMIR, A., CARTER, W. B., and HOCHMAN, R. F., Mat. Sci. Eng., v. 69, 1985, p. 89.

12. NOWAK, W. B., and SEYYEDI, J., Corrosion Division Proceedings, v. 84-3, The Electrochemical Society, Pennington, NJ, 1984, p. 89.

13. KRUGER, J., in "Electrochemistry in Industry," U. Landau, E. Yeager, and D. Kortan, eds., Plenum Press, New York, 1980, p. 317-330.

From an applications viewpoint, ion plated "thick" films ($>25 \mu\text{m}$) of Al may be the most widely used system at this time. It has been in production since 1974, and recently other coatings, such as 85% Pb/15% Sn and 90% Cu/10% Al, have been introduced.¹⁴ These have been used on steels, aluminum alloys and titanium alloys.

CONCLUSIONS

Ion plated "thick" films are successfully used for protection against corrosion. Thin ion plated films have potential applications for certain systems where an unusually high passivity results in extraordinary protection. In these cases, the appropriate composition and structure (amorphous/microcrystalline) can be conveniently obtained by ion plating, or by closely related plasma-assisted deposition techniques, provided the process parameters are suitably chosen.

14. MUEHLBERGER, D. E., and REILLY, J. J., Proceedings of the 19th Annual Airline Plating and Metal Finishing Forum, Paper P-127, SAE, Warrendale, PA, 1983.

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